Spectra of Some Alkali Salts of Hydrocarbons[1]

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Electronic absorption spectra are presented for lithium salts of fluorene, the benzofluorenes, 4,5-methylene-phenanthrene, benzanthrene, fluoradene, 9-methyl- and 9-phenylfluorene, xanthene, triphenylmethane, and tris-(p-biphenylyl)-methane in cyclohexylamine. Some cesium salts are included as well as some spectra in 1,2-dimethoxyethane and ether. The spectra are discussed in terms of simple molecular orbital theory and the cation effect and solvent effect are interpreted.

Introduction

Although increasing interest has developed in the electronic absorption spectra of organic ions,[3] only limited data are available on carbanionic species. The most extensive study of carbanion absorption spectra published so far is that of Shatenshtein and his co-workers,[4] who examined hydrocarbons in the presence of potassium amide in liquid ammonia. The spectrum of triphenylmethyl anion has long been known.[5,6] More recently, Hafner and Goliasch[7] have obtained the spectra of some polymethine carbanions, Grinter and Mason[8] have observed the spectra of additional triarylmethyl anions, and Kuhn and his co-workers[9] have reported on the anions from polyphenyl- and biphenylene-alkenes. Asami, Levy, and Szwarc[10] have reported the spectrum of benzyl anion, and Evans and George[11] have apparently obtained the spectrum of n-pentyldiphenyl-methyllithium. Finally, Waack and Doran[12] have investigated the spectra of some alkyl- and arylmethyl-lithium compounds.

In connection with a study of relative equilibrium acidities of some aromatic hydrocarbons, we have obtained the visible absorption spectra of their conjugate anions. In general, the hydrocarbons examined have $pK_a \sim 25$ on the McEwen scale,[13] and the anions can be observed only in solvents which are nonacidic, and under conditions free from oxygen, carbon dioxide, and water. Consequently, this work was carried out utilizing a high vacuum system and a glove box. Most of the hydrocarbons possess a fluorene nucleus.

Experimental

Lithium Cyclohexylamide.—A known amount of n-butyl-lithium solution in hydrocarbon solvent (Foote, Lithium Corp. of America, or synthetic)[14] was syringed into a flask flushed with purified nitrogen. The hydrocarbon solvent was removed by molecular distillation on the vacuum line. Previously fraction-ated cyclohexylamine (Eastman Kodak Co.) was vacuum trans-ferred first into a flask containing degassed Linde 4A Molecular Sieves and then into the flask containing the butyllithium. As the solution melted, butane was evolved and was removed by distillation. Solutions of 0.1 M lithium cyclohexylamide in

cyclohexylamine were water white and contained no precipitate. Lithium cyclohexylamide was also prepared by reaction of cyclo-hexylamine with ethyllithium (prepared by slight modification of the method of Talalaeva and Kocheskov[15]).

Cesium Cyclohexylamide.[16]—Cyclohexylamine purified as above was vacuum transferred into a flask containing metallic cesium. The reaction proceeded slowly with evolution of hydro-gen, giving a pale, yellow-green solution.

Spectra of Arylalkyl Anions.—All of the compounds used in this work are known. The samples obtained were purified by crystallization, chromatography, zone melting, or via the picrate; the products had sharp, correct melting points, ultraviolet spectra identical with those in the literature, and showed only one peak when analyzed by vapor phase chromatography. The ethyl ether and 1,2-dimethoxyethane used as spectral solvents were previously fractionated and vacuum transferred on the vacuum line from lithium aluminum hydride. Solutions of 0.1 M butyllithium in these ethers were made by adding the appropriate amount of butyllithium in hydrocarbon solvent to the ether.

The anion solutions were prepared by pipetting a known volume of base solution into a flask containing a weighed amount of hydrocarbon. The resulting solution was syringed into a glass-stoppered silica absorption cell. These operations were carried out in an argon atmosphere in a Kewaunee glove box. The atmosphere was kept pure by circulation over a stirred solu-tion of sodium benzophenone ketyl in tetraglyme. All glassware used in these experiments was flamed out and flushed with puri-fied nitrogen before use. The spectra were taken on a Cary Model 14 recording spectrophotometer or a Beckman DU spectrophotometer equipped with dual thermospacers using the appropriate pure solvents as reference. The results are summa-rized in Table I.

Results

Solutions of lithium cyclohexylamide in cyclohexyl-amine have appreciable absorption below about 375 $m\mu$; hence, data were obtained only in the visible re-gion (>400 $m\mu$). Except for lithium triphenylmethyl, all of the organolithium compounds examined in cyclo-hexylamine obeyed Beer's law over a concentration range greater than 50-fold.[17] In a Beer's law plot of each maximum, extrapolation to zero concentration gave zero absorbance. The anion solutions appeared to be stable; over a 2-week period there was no change in absorption. Raising the temperature from 25° to 50° caused no change in the absorption maxima.

The spectra are shown in Fig. 1–5. Extinction co-efficients at the maxima are presented in Table I for the several anions in various solvents with cesium and lith-ium cations.

Experiments in dimethoxyethane and ether and for cesium salts in cyclohexylamine were not reproduced in some cases. Consequently, the extinction coefficients determined for these conditions may not be quantita-tively reliable. However, the positions of the maxima are reproducible as shown in other experiments. The extinction coefficients for lithium salts in cyclohexyl-amine were generally reproducible to within 2% (5% maximum deviation).

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(2) (a) Alfred P. Sloan Fellow, 1958–1962; (b) National Science Founda-tion Predoctoral Fellow, 1959–1962.

(3) See S. F. Mason, Quart. Rev. (London), 15, 287 (1961), for a recent review.

(4) E. A. Izrailevich, D. N. Shigorin, I. V. Astaf'ev, and A. I. Shatensh-tein, Doklady Akad. Nauk S.S.S.R., 111, 617 (1956); I. V. Astaf'ev and A. I. Shatenshtein, Opt. Spectry. (USSR), 6, 410 (1959).

(5) L. C. Anderson, J. Am. Chem. Soc., 57, 1673 (1935).

(6) A. Hantzsch, Ber., 54, 2613 (1921).

(7) K. Hafner and K. Goliasch, Angew. Chem., Intern. Edit., 1, 114 (1962).

(8) R. Grinter and S. F. Mason, Proc. Chem. Soc., 386 (1961).

(9) R. Kuhn, H. Fischer, F. A. Neugebauer, and H. Fischer, Ann., 654, 64 (1962).

(10) R. Asami, M. Levy, and M. Szwarc, J. Chem. Soc., 361 (1962).

(11) A. G. Evans and D. B. George, Proc. Chem. Soc., 144 (1960).

(12) (a) R. Waack and M. A. Doran, Chem. Ind. (London), 1290 (1962); (b) J. Phys. Chem., 67, 148 (1963).

(13) W. K. McEwen, J. Am. Chem. Soc., 58, 1124 (1936).

(14) F. D. Hager and C. S. Marvel, ibid., 48, 2689 (1926).

(15) T. V. Talalaeva and K. A. Kocheskov, J. Gen. Chem. U.S.S.R., 23, 399 (1953); T. L. Brown and M. T. Rogers, J. Am. Chem. Soc., 79, 1859 (1957).

(16) Prepared by W. M. Padgett.

(17) Lithium triphenylmethyl did not obey Beer's law; rough calcula-tions using literature extinction coefficients[5] for the anion indicate that tri-phenylmethane and cyclohexylamine have approximately equal acidities toward lithium cyclohexylamide.

TABLE I

ABSORPTION OF ANIONS

Conjugate base from	Cation	Solvent[a]	λmax, ε				
Fluorene	Cs	CHA	447 (678)	472 (835)	504 (598)		
	Li	CHA	452 (1080)	477 (1300)	510 (827)		
	Li	Ether	415 (1010)	435 (1200)	457 (865)		
3,4-Benzofluorene	Cs	CHA		455 (2140)	477 (2430)	508 (1950)	
	Li	CHA	397 (4800)	465 (2060)	487 (2600)	519 (2040)	
	Li	DME	406 (4820)	470 (1770)	496 (2200)	533 (1640)	
	Li	Ether		420 (2310)	438 (2900)	460 (2260)	
1,2-Benzofluorene	Li	CHA	425 (8140)				
	Li	Ether	392 (9350)				
2,3-Benzofluorene	Li	CHA	420 (22000)	600 (1730)	650 (1290)		
	Li	Ether	387 (16350)	535 (1530)			
4,5-Methylenephenanthrene	Li	CHA	505 (7360)				
	Li	Ether	455 (6720)				
Benzanthrene	Li	CHA	444 (34600)	518 (5300)	550 (6400)	592 (6930)	640 (6700)
	Li	Ether	428 (19300)		540 (6520)		
Fluoradene	Li	CHA	522 (3950)	562 (4650)			
9-Methylfluorene	Li	CHA	480 (905)	512 (1130)	551 (785)		
9-Phenylfluorene	Li	CHA	452 (1950)	487 (2280)	520 (1690)		
Xanthene	Li	CHA	470 (7860)				
Triphenylmethane	Li	CHA	488[b]				
Tris-(p-biphenylyl)-methane	Li	CHA	605[c]				

[a] CHA = cyclohexylamine, DME = 1,2-dimethoxyethane, ether = diethyl ether. [b] No extinction coefficient calculated. [c] No extinction coefficient calculated; hydrocarbon dissolved slowly in cyclohexylamine.
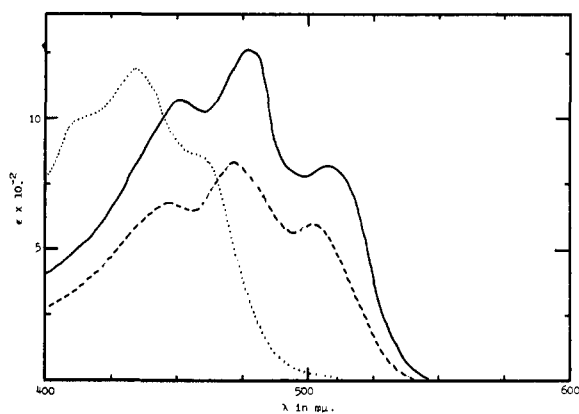

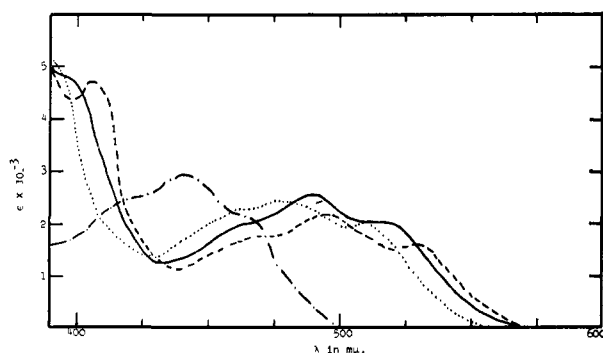Fig. 1.—Visible spectrum of fluorenyl anion: ———, Li salt in CHA; - - - -, Cs salt in CHA; · · · ·, Li salt in ether.

Fig. 2.—Visible spectrum of 3,4-benzofluorenyl anion: ———, Li in CHA; - - - -, Li salt in DME; · · · ·, Cs salt in CHA; — · — · —, Li salt in ether.

Fig. 3.—Visible spectrum of lithium salts: ———, 4,5-methylenephenanthrenyl in CHA; · · · ·, 4,5-methylenephenanthrenyl in ether; - - - -, 1,2-benzofluorenyl in CHA; — · — · —, 1,2-benzofluorenyl in ether.

Fig. 4.—Visible spectrum of lithium salts: ———, 2,3-benzofluorenyl in CHA; · · · ·, 2,3-benzofluorenyl in ether; — · — · —, benzanthrenyl in CHA; - - - -, benzanthrenyl in ether.

The solvent and cation have pronounced effects as shown in these figures. The over-all aspects of the spectrum remain constant (extinction coefficients, spacing between peaks in frequency). In accord with previous observations,[12] the maxima move to longer w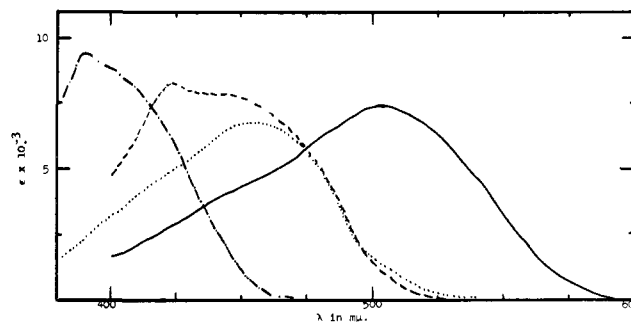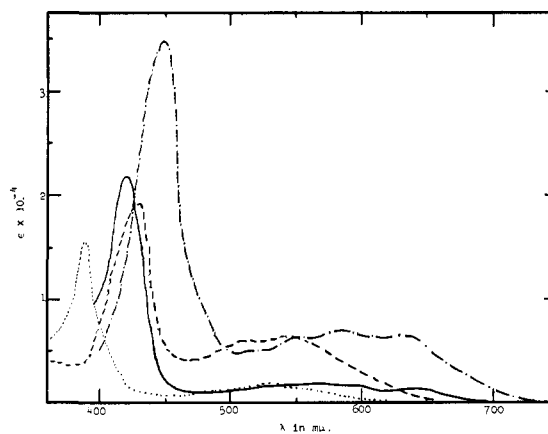ave length as the solvent becomes more "polar," but contrary to other reports,[18,19] increasing the cation radius causes shifts to shorter wave lengths.

(18) H. V. Carter, B. J. McClelland, and E. Warhurst, Trans. Faraday Soc., 56, 455 (1960).
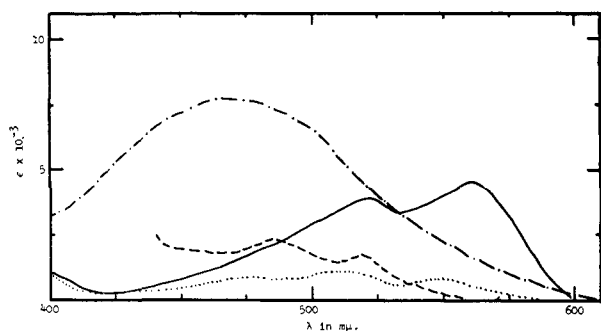(19) M. T. Jones and S. I. Weissman, J. Am. Chem. Soc., 84, 4269 (1962).

Fig. 5.—Visible spectra of lithium salts in CHA: ———,
fluoradenyl; — · — · —, xanthenyl; — — — —, 9-phenylfluorenyl;
· · · ·, 9-methylfluorenyl.

Substitution of a methyl group for hydrogen at the 9-position of lithium fluorenyl causes a red shift of 35 mμ in the long wave length absorption maxima. Again however, the over-all qualitative aspects of the spectrum remain the same (extinction and spacing).

Discussion

The Beer's law correlation indicates both that the carbanionic species are ionic in nature (presumably ion pairs) whose absorption in the concentration range examined ($\sim 10^{-3}$ M) is not a function of the concentration and that reaction 1 goes to completion, showing that these hydrocarbons are substantially more acidic than cyclohexylamine.[17]

$$C_6H_{11}NHLi + RH \longrightarrow C_6H_{11}NH_2 + RLi \qquad (1)$$
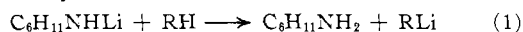
The absorption at long wave lengths and the similarity of the spectra of the lithium and cesium salts imply little covalent interaction of the ions and suggest that these carbanions are essentially planar.

The constant spacing between the long wave length bands as the solvent is changed suggests that these bands may belong to the same electronic transition and represent vibrational fine structure. This progression of bands is not unlike that in the spectra of aromatic hydrocarbons. The long wave length absorption in conjugated anions and cations is usually associated with transition of an electron from the highest occupied to lowest vacant MO similar to the para-bands of polycyclic aromatic hydrocarbons.[12b,20,21] Meuche, Strauss, and Heilbronner,[22] for example, have shown how the transition energies for various tropylium cations correlate well with the orbital energies calculated by the HMO method. Although we expect to present a more detailed theoretical discussion of our anion spectra in a subsequent paper, it is convenient to examine here the application of the simple HMO method to our results. Because the spectra are dependent on solvent and cation (vide infra), only our results for lithium salts in cyclohexylamine are used in the experimental and HMO transition energies in Table II and Fig. 6.

Several of the compounds form a fair correlation that is suitable for discussion purposes. The deviation of fluoradene may be associated with the high strain in this anion. The larger deviations of 1,2-benzofluorene and 4,5-methylenephenanthrene do not seem to be explicable on this basis; both of these anions have broad featureless spectra (Fig. 3) and the apparent maxima in these cases may not correspond to the theoretical transition assumed. If, in these two cases, the observed λ_{max} corresponds to a Frank–Condon transition to higher vibra-

(20) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(21) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962.

(22) D. Meuche, H. Strauss, and E. Heilbronner, Helv. Chim. Acta, 41, 57 (1958).
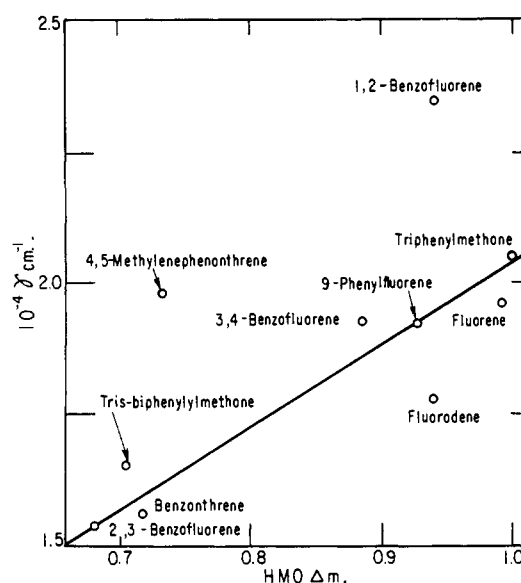
Fig. 6.—Correlation of absorption maxima of lithium salts of hydrocarbons in cyclohexylamine with HMO transition energies.

tional levels of the excited state, the O → O transition would occur at longer wave lengths—a direction consistent with the observed deviations from the MO correlation.

TABLE II
TRANSITION ENERGIES FOR LITHIUM SALTS IN CYCLOHEXYLAMINE

Lithium salt of	λ_{max}, mμ	$10^{-4}\nu$, cm.$^{-1}$	$\frac{m_{m+1} -}{m_m}$
Fluorene	510	1.960	0.993
3,4-Benzofluorene	519	1.926	.886
1,2-Benzofluorene	425	2.352	.940
2,3-Benzofluorene	650	1.539	.681
4,5-Methylenephenanthrene	505	1.980	.734
9-Phenylfluorene	520	1.924	.927
Benzanthrene	640	1.562	.718
Fluoradene	562	1.780	.940
Triphenylmethane	488	2.050	1.000
Tris-(p-biphenylyl)-methane	605	1.653	0.705

HMO interpretations do serve to help explain several noteworthy features of our results; for example, the effect on the spectrum of fluorenyl anion of alkyl substitution in the 9-position. The HMO calculations[23] indicate that the charge density at the 9-position of fluorenyl anion is greater in the ground state than in the first excited state ($c_m^2 > c_{m+1}^2$). Since a methyl group is electron donating, it would be expected to destabilize the ground state more than the excited state, causing a shift to longer wave lengths.[24]

Waack and Doran[12b] have observed a bathochromic shift as the solvent dielectric constant or basicity is increased; they suggest that this result is caused by the polarizability and dipole orientation of the solvent or by increased ionization of the carbon-metal bond. The effect of solvent in our system is consistent with this observation; in our interpretation, however, we emphasize the importance of cation solvation. Cyclohexylamine and dimethoxyethane are good solvents for cations; for example, radical anions are easily formed in amines and ethers of these types, presumably because of the favorable solvation energy of the cation. Consider the ion pair as a dipole in both

(23) A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, New York, N. Y., in press.

(24) A more complete discussion of this type of phenomenon can be found in ref. 20 and 21.

RL: RCs

g

g

s

EXCITED
STATE

ΔE^*_g s ΔE^*_g ΔE^*_s

ΔE^*_s

GROUND
STATE   g   g

s   s

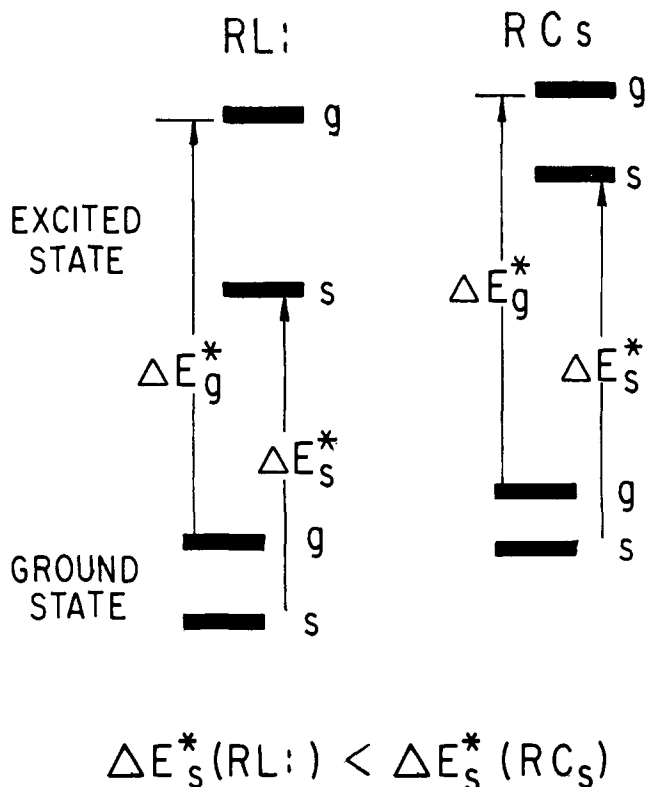$$\Delta E^*_s (RL:) < \Delta E^*_s (RC_s)$$

Fig. 7.—Schematic explanation of the effect of solvent on transition energies of lithium and cesium salts of hydrocarbons.

the ground state and the excited state, the cation being the positive end of the dipole. In the excited state with its new charge distribution, the dipole moment becomes larger—the ion pair in the ground state has the cation situated so as to provide the smallest dipole; the excited state has a greater dipole, assuming that the total negative charge remains constant and the cation does not move (Franck–Condon principle). Simple MO calculations[23] indicate that the charge moves from the benzylic position in the ground state to the ring in the excited state. The negative charge is spread out in the organic molecule and is relatively unaffected by solvent; however, the positive charge is concentrated on the metal ion. Since the dipole is larger in the excited state, solvation will become more important. Hence, "polar" solvents stabilize the cation more in the excited state, resulting in lower energy and absorption at longer wave length. Ethyl ether is a "nonpolar" solvent in this context because it is considerably less effective at stabilizing positive ions than are the less sterically hindered tetrahydrofuran and the dimethyl polyglycol ethers.

Cation solvation also serves to interpret the result we find in changing the metal ion. Carter, McClelland, and Warhurst[18] found that the absorption maxima of some metal ketyls in dioxane shifted to longer wave length as the cation radius increased. Similarly, Jones and Weissman[19] observed red shifts in the spectrum of tris-p-nitrophenylmethide ion as the cation was changed from sodium to potassium. These results differ in direction from our findings in which for *hydrocarbon* anions in cyclohexylamine a 5 to 10 mμ *blue* shift is observed in changing the cation from lithium to cesium (Fig. 3). This observation appears to be inconsistent with the hypothesis that tighter ion pairs absorb at shorter wave length[12,19]; the lithium salts would be expected to be less dissociated than cesium salts.

Lithium cation has a smaller volume than does cesium cation and is well known to have a larger solvation energy. In the excited state, both cations have greater solvation energy, but the lithium cation gains more solvation stabilization than does cesium. Hence, the lithium salts of our hydrocarbons have lower transition energies and absorb at longer wave length than the corresponding cesium compounds. This argument is shown schematically in Fig. 7. In the vapor state, the metal cation is "solvated" only by the hydrocarbon anion. Such bonding is greater for Li^+ than for Cs^+. In solution, the solvation energy of the cation is greater for he more polar excited state than for the ground state, but the difference is larger for lithium. Hence, ΔE^* (RCs) $- \Delta E^*$(RLi) is expected to be negative in the vapor or in nonpolar solvents and become more positive in polar solvents.

Even relative magnitudes of these shifts are explicable on this basis. HMO calculations[23] show that most of the charge in fluorenyl and 3,4-benzofluorenyl anions is in the benzylic positions; hence, the ground states of cation ion pairs of both anions would be expected to have comparable dipole moments—assuming that the cation is close to the benzylic position. In the excited states, however, 3,4-benzofluorenyl anion has substantial charge in the benzo-ring; hence, the change in its ion pair dipole moment between ground state and excited state should be greater than that for fluorenyl. Consequently, the transition energy for 3,4-benzofluorenyl should be more sensitive to the cation and cation solvation than should fluorenyl. Our experimental results show that the cesium–lithium shift is, indeed, greater for 3,4-benzofluorenyl than for fluorenyl.

This interpretation contrasts with others. Carter, McClelland, and Warhurst[18] attribute the red shifts in the spectra of ketyls with increasing ionic radius of the cation to perturbation by the cation of the hydrocarbon molecular orbitals. Kuwata[25] explained shifts of the same sort by a charge transfer effect. However, most of the other results of changing the cation were observed in systems containing oxygen—ketyls or nitro-substituted arylmethyl ions. In these systems, neither the position of maximum charge density nor the location of the metal ion can be inferred; hence, the solvation argument we propose cannot be applied to these cases in as straightforward a manner as for hydrocarbons.

(25) K. Kuwata, *Bull. Chem. Soc. Japan*, **33**, 1091 (1960).